

The University of Chicago

**THE PREPARATION AND STUDY OF
THE HALIDES AND A NITRIDE
OF GALLIUM**

**A DISSERTATION SUBMITTED TO THE
GRADUATE FACULTY IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY**

DEPARTMENT OF CHEMISTRY

**By
JAMES BAYARD PARSONS**

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AUGUST 1931



THE PREPARATION OF GALLIUM TRIBROMIDE AND GALLIUM TRIIODIDE*

BY JAMES B. PARSONS

Lecoq de Boisbaudran and E. Jungfleisch¹ announced many years ago that metallic gallium reacts with chlorine, bromine and iodine to form the corresponding halides. They described the relative intensities of the reactions as being in the usual order, and the boiling points and melting points of the compounds as increasing with increasing atomic weight of the halogen. Shortly following this announcement, Lecoq de Boisbaudran² made a very brief statement regarding the preparation of several chlorides, bromides and iodides of gallium. He later showed that two chlorides of gallium, namely, gallium dichloride³ and gallium trichloride,⁴ are readily formed by the direct combination of the elements. The existence of these two chlorides was substantiated by quantitative data. Although the reactions of bromine and iodine with metallic gallium are described by this investigator, there is no evidence to show that these halides were ever analyzed or studied, nor is any mention made of the technique employed in their preparation. According to the literature no attempts have ever been made to prepare a fluoride of gallium.

In the present investigation gallium tribromide and gallium triiodide are prepared and some of the physical properties of the compounds are determined in order to further our knowledge of the chemistry of this relatively unknown element. Qualitative experiments are carried out to show that a fluoride of gallium exists.

Source of Material

The gallium used in the investigation was obtained from the mineral germanite⁵ whose gallium content varies from 0.5-0.75 percent.⁶ After the germanium⁷ had been removed from the mineral, the gallium was extracted with hydrochloric acid according to the procedure of Kraus, Johnson and Foster.⁸ In order to obtain a pure product, the gallium hydroxide was reprecipitated several times by means of sodium acid sulfite. The hydroxide

* Contribution from the Kent Chemical Laboratory of the University of Chicago.

¹ Lecoq de Boisbaudran and E. Jungfleisch: *Compt. rend.*, **86**, 577 (1878).

² Lecoq de Boisbaudran: *Compt. rend.*, **86**, 756 (1878).

³ Lecoq de Boisbaudran: *Compt. rend.*, **93**, 294 (1881).

⁴ Lecoq de Boisbaudran: *Compt. rend.*, **93**, 329 (1881).

⁵ Pufahl: *Metall. u. Erz.*, **19**, 324 (1922); Kriesel: **20**, 257 (1923).

⁶ Kriesel: *Chem. Ztg.*, **48**, 961 (1924); Lunt: *S. African J. Sci.*, **20**, 157 (1923); Kiel: *Z. anorg. Chem.*, **152**, 101 (1926).

⁷ A pyrogenic process for the removal of germanium from germanite ore was described by Kraus and Johnson at the Swampscott Meeting of the American Chemical Society, September, 1928.

⁸ A report of this extraction process was given by L. S. Foster at the Swampscott Meeting of the American Chemical Society, September, 1928. The results of the methods for both germanium and gallium will constitute the subjects of forthcoming publications.

was dissolved in potassium hydroxide and the solution was electrolyzed.⁹ Metallic gallium collected at the cathode as a small metallic-appearing ball which dropped into a cup below the electrode. Although the electrolysis was carried out at room temperature, sufficient heat was generated at the cathode to keep the metal in a molten condition. (The melting point of gallium is 29.75°). The gallium was purified by fractional crystallization on a platinum wire from the supercooled liquid metal.¹⁰

Gallium Tribromide

Preparation. Gallium tribromide was prepared by the direct combination of the elements in vacuo. Metallic gallium (about 1 g.) was introduced into a Pyrex tube as one solid piece. As soon as the tube was sealed off, the entire system was evacuated by means of a mercury vapor pump supported by a Hy-Vac oil pump. Liquid bromine, which had previously been twice distilled from phosphorus pentoxide, was then distilled in vacuo into the tube containing the gallium which was cooled to -33.5° by means of a Dewar flask of liquid ammonia.

The gallium reacted with the bromine very rapidly at the temperature of the boiling point of liquid ammonia. At room temperature and even at 0° , the metal reacted on the surface of the liquid bromine in much the same manner as does an alkali metal on the surface of water. A considerable amount of energy was liberated both in the form of heat and light. When the initial and more vigorous reaction was over, the mixture was allowed to stand for two days to insure complete reaction, the excess bromine was removed by condensation into a small side tube, which was then sealed off from the main reaction tube, and finally the entire system was evacuated to a pressure of 0.001 mm. Under this low pressure the salt began to sublime at 90° into the neck of the reaction tube. This process was greatly hastened by increasing the temperature to about 125° . When the major part of the salt had

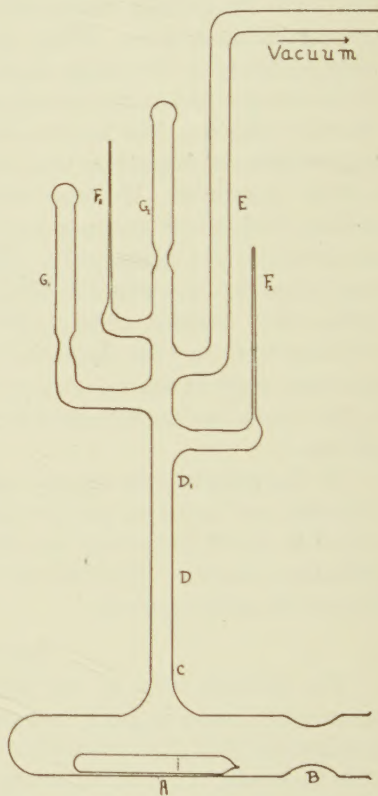


FIG. 1.
Apparatus for the Sublimation of
Gallium Tribromide and Gallium
Triiodide.

⁹ No definite procedure was followed in the electrolysis of this alkaline solution. The current density was varied to obtain the greatest yield of metal, but the results were found to be quite inconsistent even when the same conditions were thought to have been employed in different experiments.

¹⁰ Richards and Boyer: J. Am. Chem. Soc., 43, 274 (1921).

sublimed into a limited space in the tube, it was sealed off from the system. This tube, containing the gallium bromide, was scratched with a file, cracked slightly with a fine hot glass rod, and then introduced into a larger tube, A, as shown in Fig. 1. After sealing off the system at B, the entire apparatus was exhausted to a low pressure. The tube containing the salt was then broken by applying a slight jar in the vicinity of A. A Crisco bath was placed about the apparatus and heated to 140° at which temperature sublimation of the salt into D took place rapidly. Then A was removed by sealing off at C. The smaller tube D was of such a length as to allow for several successive sublimations. The tube was finally sealed off at D₁ and the salt was then sublimed into the various branches above. F₁ and F₂ represent melting point tubes while G₁ and G₂ are small tubes to collect samples of the salt for analysis. During the process of sublimation some of the salt appeared in E. It was thus possible to obtain several small samples of the bromide of high purity for carrying out analyses and determining some of its physical properties.

Analysis. A sample of the salt which had been sublimed several times was sealed off in a tube (G₁, Fig. 1). The tube was scratched, washed with alcohol and ether and then weighed. It was broken and then dropped immediately into water where the salt dissolved quickly. The parts of the tube were removed, washed, dried and weighed in order to obtain the weight of the dissolved salt. Two aliquot parts of the solution were analyzed for bromine by the usual gravimetric method of precipitation as silver bromide.

Anal. Subs., 0.3226, 0.3893: AgBr, 0.5861, 0.7072. Calc. for GaBr₃: Br, 77.47. Found: 77.31, 77.31.

The third aliquot sample was analyzed for gallium by precipitation of the hydroxide with ammonium acid sulfite according to the procedure described by Porter and Browning.¹¹

Anal. Subs., 0.3642. Ga₂O₃, 0.1098. Calc. for GaBr₃: Ga, 22.53. Found: 22.43.

Melting Point. Several melting point determinations were carried out with three different samples of gallium tribromide and in each case a value of 122.5 was obtained.

Density. The density of gallium tribromide was determined at 120° and at 125° . Ordinary methods could not be used due to the hygroscopic nature of the salt and the small quantity available. Nor was it found feasible to determine the density of the solid salt as it showed a marked tendency to contract from the walls of glass upon solidification. It was accordingly found necessary to determine the density of the fused substance. This was accomplished by comparing the weight of the melted salt at 120° and 125° with the weight of an equal volume of mercury at the same temperatures.

The mercury was purified according to the method of Hulett and Minchin.¹² The gallium bromide was subjected to several sublimations for

¹¹ Porter and Browning: J. Am. Chem. Soc., 41, 1491 (1919).

¹² Hulett and Minchin: Phys. Rev., 21, 389 (1905).

purification and then sealed in Pyrex capillary tubes of uniform bore. The inner diameter of the capillary tube was determined by weighing a given length of mercury, the length being measured with a travelling microscope. The menisci were read with a cathetometer. A meniscus correction was applied by assuming a value of one-third the radius of the tube for the height above the bottom of the meniscus. The following values for the density were obtained:

Diameter of Tube	Temperature	Density
0.1205 cm.	120°	3.123
0.1215	120	3.138
0.1205	125	3.095
0.1215	125	3.109

Other Properties. Gallium tribromide is a white crystalline substance melting at 122.5°. It dissolves readily in water undergoing hydrolysis. It is exceedingly hygroscopic. The salt begins to sublime at 90° when subjected to a pressure of 0.002 mm. No decomposition occurs when it is sublimed and melted. When melted and then allowed to cool, it appears to supercool several degrees.

In the initial preparation of gallium tribromide a residue remained in the reaction tube which did not sublime with the bulk of the material. When it was subjected to a much higher temperature, about 200°, a small quantity of a white salt appeared on the walls of the tube above the bath. This substance may be a lower bromide of gallium due to a reaction between the normal bromide and free gallium. Its properties will be described in a later paper.

Gallium Triiodide

Preparation. This salt was likewise prepared by the direct union of the elementary constituents. Resublimed iodine was dried for several days over phosphorus pentoxide. The metallic gallium was purified by crystallization. Equivalent quantities of these two elements were reacted in a small Pyrex tube in the absence of air and moisture. Reaction did not take place at room temperature;¹³ however, on warming gently with a flame, a vigorous reaction followed with the evolution of much heat and light. A crust of the iodide, which appeared to form on the surface of the small pieces of metallic gallium, was removed by shaking the tube and subsequent heating. By repeating this process several times, it was found possible to complete the reaction. The tube was then cracked and placed in a larger tube, A, as shown in Fig. 1. Several sublimations of the salt were carried out to obtain samples of a pure product. The same general procedure was followed as in the case of gallium tribromide.

Analysis. Two samples were analyzed for iodine by the usual method of precipitation as silver iodide.

¹³ Reaction would undoubtedly have taken place here providing the constituents were in a finely divided condition.

Anal. Subs., 0.0290, 0.1604: AgI, 0.0453, 0.2505. Calc. for GaI_3 : I, 84.53. Found: 84.44, 84.42.

The gallium was determined by precipitation of the hydroxide with ammonium acid sulfite and weighed as Ga_2O_3 according to the previously described procedure.

Anal. Subs., 0.3300, 0.2521: Ga_2O_3 , 0.0690, 0.0516. Calc. for GaI_3 : Ga, 15.47. Found: 15.55, 15.58.

Melting point. The melting point of gallium triiodide was found to be at 213.5° . A slight amount of decomposition evidently takes place at this temperature since the liquid appears darker than the original salt. The color, amber to red, is probably due to the presence of a small amount of free iodine.

Color. Gallium triiodide is a lemon yellow crystalline substance at ordinary temperatures. Lecoq de Boisbaudran undoubtedly obtained a colored salt by reacting iodine with gallium since he makes the statement that it would, without doubt, be colorless if it were pure. Whether or not he obtained a pure product is not known; he gives no analytical data to support his description of the salt. We have carried out several preparations of gallium triiodide and in each instance a light yellow salt was obtained even after it had been subjected to several sublimations. Some of the small tubes of the iodide were broken under a starch solution and in no case was a test obtained for the presence of free iodine. However, when this solution was allowed to stand for a few hours, free iodine was found, due to the hydrolysis of the salt and subsequent decomposition of hydriodic acid.

Other Properties. Gallium triiodide sublimes readily in vacuo at a temperature as low as 160° . It hydrolyzes readily and is hygroscopic. When it is exposed to the air iodine fumes are liberated and the residue appears to be much darker than the original salt. At higher temperatures decomposition takes place.

Gallium Fluoride

When a small quantity of metallic gallium was treated with hydrofluoric acid (50% solution) in a platinum crucible, a white substance, insoluble in an excess of acid and of much greater volume than the original amount of metal, was formed. The reaction was allowed to continue for several hours and the excess of acid was evaporated over steam. The white residue gave tests for fluorine. The details of the preparation and properties of this substance will be described in a later article.

Summary

Gallium tribromide and gallium triiodide have been prepared by the direct combination of the elements. Some of the physical properties of these salts have been determined.

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NITROGEN COMPOUNDS OF GALLIUM

- I. The Ammonates of Gallium Tribromide and Gallium Triiodide
- II. Gallium Trifluoride Trihydrate and its Reaction with Ammonia*

BY JAMES B. PARSONS

The halides of the elements of the third group, namely, boron, aluminium, gallium, indium and thallium, appear to show divergent properties in their behavior toward ammonia. In general, the halide reacts with ammonia gas or liquid ammonia to form an addition compound (ammonate). As an alternative, the halide may be partially or completely ammonolyzed with the formation of the ammonium salt of the halogen and the amide or imide of the metal. Whether or not the ammonolytic reaction will proceed is dependent in a large measure upon the nature of the cation in combination with the halogen.

Boron trifluoride¹ combines with one molecule of ammonia to form an ammonate which has recently been shown to be appreciably ammonolyzed² in liquid ammonia solution. The trichloride,³ tribromide⁴ and triiodide⁵ of boron form ammonates with ammonia at low temperatures but readily undergo ammonolysis at slightly elevated temperatures. All the halides of aluminum^{6,7,8} form ammonates with no indication of ammonolysis. The corresponding salts of indium⁹ and thallium,¹⁰ with the exception of the fluorides, behave similarly.

Gallium occupies an intermediate position in the third group of elements. Since it is more electropositive in nature than aluminium, one would predict its salts to be stable in liquid ammonia, particularly at low temperatures. The following work was undertaken to determine some of the properties of the halides of gallium in liquid ammonia solution.

Experimental

The halides of gallium were prepared by the direct combination of the elements according to a previously described method.¹¹ The tribromide and triiodide of gallium were selected since appreciable quantities of these salts were available. Liquid ammonia, dried over sodium in small steel cylinders, was employed in all experiments.

* Contribution from the George Herbert Jones Laboratory of the University of Chicago.

¹ Mixer: *Am. Chem. J.*, **2**, 153 (1880).

² Kraus and Brown: *J. Am. Chem. Soc.*, **51**, 2690 (1929).

³ Joannis: *Compt. rend.*, **135**, 1106 (1902).

⁴ Besson: *Compt. rend.*, **112**, 1002; **113**, 78 (1891); Stock: *Ber.*, **34**, 949 (1901).

⁵ Besson: *loc. cit.*; Joannis: *loc. cit.*

⁶ Clark: *Am. J. Sci.*, (5) **7**, 1 (1924).

⁷ Mellor: "Comprehensive Treatise on Inorganic and Theoretical Chemistry," **5**, 319-20, 326 (1924).

⁸ Franklin: *J. Am. Chem. Soc.*, **27**, 847 (1905).

⁹ Klemm: *Z. anorg. Chem.*, **163**, 240 (1927).

¹⁰ Biltz and Stollenwerk: *Z. anorg. Chem.*, **119**, 97 (1921).

¹¹ Johnson and Parsons: *J. Phys. Chem.*, **34**, 1210 (1930).

Gallium Tribromide Hexammonate.

Dry ammonia gas was condensed at -33.5° on gallium tribromide in a tube which could be readily detached from a "vacuum line" and weighed. The usual technique was employed to prevent contact of the salt with air and moisture. Reaction followed immediately after the introduction of ammonia to produce a white powder which appeared to be only slightly soluble in liquid ammonia. After the mixture had been allowed to stand in contact with the ammonia for several hours, the excess ammonia was allowed to escape and the system was thoroughly evacuated. The tube and contents finally assumed a constant weight at room temperature. The following results were obtained for two different preparations.

TABLE I

The Formation of Gallium Tribromide Hexammonate

Weight of GaBr ₃ grams	Weight of ammonia reacted (grams)	Ratio NH ₃ /GaBr ₃ found
0.4865	0.1632	6.09
0.4690	0.1533	5.94

Although ammonia was removed from the compound in vacuo until the weight of the tube and contents assumed a constant value and the pressure was reduced to 10^{-4} mm., its odor could be detected when the ammonate was exposed to air. A sample of the material after exposure to air, was analyzed for ammonia by distillation from an alkaline solution into standard acid solution, and for bromine by the usual procedure. The ammonia content was found to correspond to approximately two-thirds of the total amount that had reacted with the gallium tribromide, while the bromine analysis agreed well with the calculated value.

Anal. Subst., 0.0553; NH₃, 0.0099; AgBr, 0.0756. Calcd. for GaBr₃.6NH₃, NH₃, 24.82; Br, 58.24. Found: 17.94, 58.17.

These facts indicate that while ammonia is lost on exposure of the ammonate to air, water replaces the ammonia so that the net change in weight is very small. However, this process was found to be readily reversible. When the material was again subjected to liquid ammonia and the excess ammonia removed as described above, analysis showed six molecules of ammonia to be in combination with the gallium tribromide.

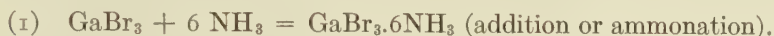
In order to obtain pure samples of the ammonate for analysis, they were sealed off in small tubes attached to the reaction tube without exposure to the air. The tubes were then cracked with a piece of hot glass and finally broken in a Kjeldahl flask under the alkali solution. The results recorded below were obtained on two samples of the ammonate; sample I was exposed to air and then treated with liquid ammonia to restore the ammonate to its original condition, while sample II was prepared and manipulated in the absence of air and moisture.

Anal. Subst., I, 0.1062, II, 0.6221; NH₃, 0.0263, 0.1531. Calcd. for GaBr₃.6NH₃, NH₃, 24.82. Found: 24.74, 24.62.

Sample I was analyzed for bromine by the usual method.

Anal. Subst., 0.1062; AgBr, 0.1453. Calcd. for $\text{GaBr}_3 \cdot 6\text{NH}_3$; Br, 58.24; Found: 58.22.

While the above values show the quantity of ammonia absorbed in the reaction, they do not indicate the nature or mechanism of the process. There are two possibilities:



If ammonolysis were to take place, the ammonium bromide, which is highly soluble in liquid ammonia, could be readily separated from the slightly soluble product of the reaction (presumably the amide or imide of gallium). Attempts to carry out such a separation were made as follows: a Pyrex tube about 1.5 cm. in diameter and 15 cm. in length was fitted with a side arm stopcock and a second leg of the same dimensions. A small amount of gallium tribromide was placed in the tube which was then sealed off and evacuated. Ammonia was condensed on the salt and the system was allowed to stand for several hours. The clear solution above the salt was carefully decanted into the second leg of the tube. A Dewar flask of ammonia was placed about the main portion of the tube and the ammonia distilled out of the leg to the original sample with the deposition of any material that may have dissolved. Ten such extractions were made until a quantity of the soluble portion sufficient for an analysis was obtained. An examination of this material proved it to be identical with gallium tribromide hexammonate. This experiment shows that ammonolysis does not take place and that the solvated salt is slightly soluble in liquid ammonia.

Additional proof for this result is based upon the fact that ammonium bromide is an acid in liquid ammonia and, when treated with a strongly electro-positive metal such as sodium, liberates hydrogen according to the following equation:



Experiments showed, however, no indication of hydrogen gas when metallic sodium was added to a solution of gallium bromide in liquid ammonia. On the other hand, reduction of the salt to metallic gallium appeared to take place. According to the results of these experiments it is concluded that an ammonate, $\text{GaBr}_3 \cdot 6\text{NH}_3$, is formed when gallium tribromide is subjected to liquid ammonia.

Properties. The ammonate is obtained as a white powder from liquid ammonia solution. In the absence of moisture it is remarkably stable. In moist air, water molecules replace the ammonia which is readily liberated as a gas. This process is found to be reversible; in other words, ammonia will replace the water in liquid ammonia solution. Dry air does not appear to have any effect upon the ammonate. It is easily soluble in alkali and hydrochloric acid solutions. At higher temperatures, about 100°C , the ammonate slowly loses ammonia when subjected to a high vacuum. The ammonate exhibits an appreciable solubility in liquid ammonia.

Gallium Triiodide Hexammonate.

Gallium triiodide was treated with liquid ammonia in a manner analogous to that employed in the bromide investigation described above. A reaction was found to proceed rapidly with the formation of gallium triiodide hexammonate as is indicated by the following results:

TABLE II

The Formation of Gallium Triiodide Hexammonate

Weight of GaI ₃ , g.	Weight of ammonia reacted, g.	Ratio NH ₃ /GaI ₃ found
0.8728	0.1981	6.00
0.5087	0.1142	5.94

When the ammonate was exposed to air, ammonia was liberated but was found to be restored as in the case of the bromide by a second treatment with liquid ammonia. The product exposed to air was analyzed for ammonia:

Anal. Subst., 0.3351. NH₃, 0.0549. Calcd. for GaI₃.6NH₃: NH₃, 18.40. Found: 16.39.

Another portion of the product exposed to air was restored to its original condition in liquid ammonia, the ammonate was freed of the excess ammonia and finally analyzed.

Anal. Subst., 0.2430; NH₃, 0.0453. Calcd. for GaI₃.6NH₃: NH₃, 18.40. Found: 18.64.

A third sample was prepared and analyzed in the absence of air and moisture.

Anal. Subst., 0.6246; NH₃, 0.1159. Calcd. for GaI₃.6NH₃: NH₃, 18.40. Found: 18.55.

Analyses were not made here for gallium and iodine since the samples of the triiodide were taken from a larger lot which had been carefully purified and analyzed (see ref. 11).

The increase in weight, as given in Table II, and the ammonia analyses show six molecules of ammonia in combination with one gram molecule of gallium triiodide. The ammonate was found to possess properties similar to those of the corresponding bromide salt.

II. Gallium Trifluoride Trihydrate and its Reaction with Ammonia

The third group elements boron, aluminium, indium and thallium are known in combination with fluorine. According to the literature, no attempts have been made to study the reactions of gallium with fluorine and fluorides. The present authors¹¹ observed that metallic gallium reacts readily with hydrofluoric acid (50% solution) to produce a white substance, insoluble in excess acid and of much greater volume than the original amount of metal. In the present investigation, this reaction has been studied in more detail to show that the product is a hydrated fluoride of gallium, GaF₃.3H₂O. This hydrated salt is also studied in the liquid ammonia solution.

Gallium Trifluoride Trihydrate.

The hydrated salt was prepared by two methods, namely, (A) by a reaction of metallic gallium with hydrofluoric acid (50% solution) and (B) by a reaction between gallic oxide and hydrofluoric acid (50% solution).

(A). A small amount of metallic gallium was treated with hydrofluoric acid in a platinum crucible. Reaction followed immediately to produce a white substance which appeared to be insoluble in the acid. The reaction was hastened considerably by making contact between the metallic gallium and the crucible with a piece of platinum wire. After the reaction was allowed to proceed in this manner for several hours, the excess acid was removed by evaporation over a steam bath. The increase in weight of the product over that of the metal suggests the formation of $\text{GaF}_{3.3}\text{H}_2\text{O}$ as is shown in the following table.

In each case the actual yield of the product was slightly less than that calculated for $\text{GaF}_{3.3}\text{H}_2\text{O}$. It was noticed, however, that during the reaction and the evaporation of the excess acid, a small amount of the solution was carried out of the crucible in the spray of escaping hydrogen and hydrogen fluoride.

TABLE III

Preparation of Gallium Trifluoride Trihydrate

Weight of gallium, grams	Weight of salt obtained, grams	Weight calc. for $\text{GaF}_{3.3}\text{H}_2\text{O}$.
0.4858	1.2347	1.2590
0.8155	2.0644	2.1149
0.5418	1.3933	1.4055

Analysis. Two samples of the salt, each from a different preparation, were analyzed for gallium and fluorine. For the gallium analysis, the salt was dissolved in dilute hydrochloric acid, gallium hydroxide was precipitated with ammonium acid sulfite,¹² and the hydroxide was ignited and finally weighed as gallic oxide.

Anal. Subst., 0.2239, 0.2959; Ga_2O_3 , 0.1160, 0.1539. Calcd. for $\text{GaF}_{3.3}\text{H}_2\text{O}$; Ga, 38.57. Found: 38.54, 38.69.

For the fluorine analysis, the method of Starck and Thorin¹³ was used with slight modification.¹⁴ The fluorine was precipitated as calcium fluoride which was found to be exceedingly difficult to filter on account of its gelatinous structure. Accordingly, the calcium fluoride was precipitated and weighed with a known amount of calcium oxalate. A weighed quantity of sodium oxalate was added to the solution slightly acidified with acetic acid; to this solution was added an excess of calcium chloride. The precipitate was dried at 210° and the weight of calcium oxalate was deducted to give that of the calcium fluoride.

Anal. Subst., 0.3325, 0.2269; CaF_2 , 0.2152, 0.1483. Calcd. for $\text{GaF}_{3.3}\text{H}_2\text{O}$; F, 31.53. Found: 31.51, 31.82.

¹² Porter and Browning: J. Am. Chem. Soc., **41**, 1491 (1919).

¹³ Starck and Thorin: Z. anal. Chem., **51**, 14 (1912).

¹⁴ Sodium oxalate was substituted for oxalic acid.

(B). A more convenient method of preparation of the hydrated fluoride was found in the treatment of gallic oxide with hydrofluoric acid (50% solution).¹⁵ The oxide is readily soluble in this acid solution. When the excess acid is removed by evaporation, $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$ is obtained as a fine white powder. The results of this reaction are given in Table IV; the analyses are recorded below.

TABLE IV

Preparation of Gallium Trifluoride Trihydrate

Weight of Ga_2O_3 , grams	Weight of salt obtained, grams	Weight calc. for $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$, gram
0.1986	0.3756	0.3829
0.4019	0.7728	0.7749
0.3066	0.5875	0.5912

Anal. Subst., 0.5875, 0.5799. Ga_2O_3 , 0.3066, 0.3003. Calcd. for $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$; Ga, 38.57. Found: 38.83, 38.53.

Properties. Gallium trifluoride trihydrate is a fine white powder as prepared by the above described methods, insoluble in cold water but appreciably soluble in hot water. It is readily soluble in dilute hydrochloric acid and sparingly soluble in hydrofluoric acid (50% solution). It is stable in air; a sample exposed to the atmosphere for several weeks showed no change in appearance or weight. When heated to 140° in a vacuum under the influence of an oil pump and Hg-vapor pump, water is slowly liberated. One-half of the water (1.5 mols) appears to be liberated much more easily than the remaining water molecules.¹⁶

The Action of Ammonia on Gallium Trifluoride Trihydrate. The hydrated fluoride was treated with liquid ammonia in a weighed, evacuated tube in a manner analogous to that employed in the preparation of the gallium bromide and gallium iodide ammonates. The system was evacuated to constant weight at room temperature. A white powder similar in appearance to the original salt resulted. The product was analyzed for ammonia and gallium according to the usual procedures which have already been described.

Anal. Subst., 0.3341, 0.0872; NH_3 , 0.0476, 0.0122. Calcd. for $\text{GaF}_3 \cdot 3/2 \text{H}_2\text{O} \cdot 3/2 \text{NH}_3$; NH_3 , 14.23. Found: 14.25, 14.02.

Anal. Subst., 0.0853, 0.0825; Ga_2O_3 , 0.0445, 0.0432. Calcd. for $\text{GaF}_3 \cdot 3/2 \text{H}_2\text{O} \cdot 3/2 \text{NH}_3$; Ga, 38.84. Found: 38.81, 38.95.

The analyses suggest strongly that half of the water of the trihydrate is replaced by ammonia molecules. This result is in accord with the fact that half of the water of the trihydrate is easily removed when the salt is subjected to a high vacuum at 140° , while the remaining water molecules are removed with great difficulty at this temperature under the same conditions. The results merely suggest the empirical formula given above as one possibility since the molecular weight of the complex is not known.

¹⁵ Observations by Mr. M. C. Crew.

¹⁶ Observations by Mr. M. C. Crew. The details of the dehydration of $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$ will appear in a later paper on the preparation of anhydrous gallic fluoride.

The addition of ammonia to the anhydrous gallic fluoride might produce results of an entirely different nature. Studies are now being made in this direction.

Summary

Gallium tribromide and gallium triiodide react with liquid ammonia at -33.5° to form ammonates in which six molecules of ammonia are combined with the halide. The ammonates are stable at room temperature in the absence of moisture. It is shown that ammonia is readily displaced by water molecules when the ammonates are exposed to air. This process is found to be readily reversed in liquid ammonia.

The halides of gallium resemble those of indium and aluminium in their behavior with ammonia.

Two methods are given for the preparation of gallium trifluoride trihydrate.

The hydrated trifluoride is studied in liquid ammonia solution. A complex is formed in which one-half of the water is replaced by ammonia molecules.

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NITROGEN COMPOUNDS OF GALLIUM

III. Gallic Nitride*

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Introduction

A nitride of each member of Family B, Group III, of the periodic system with the exception of gallium has been reported in the literature. Boron nitride has been prepared by several different methods. Stock and Blix¹ obtained the nitride by the decomposition of boron imide; Meyer and Zappner² passed a mixture of boron trichloride and ammonia through a tube heated at high temperatures and obtained boron nitride of high purity; and Friederich and Sittig³ have reported the formation of the compound through the direct combination of its elements at 1200°. It is described by several workers as an exceedingly stable compound. Aluminium has been shown to combine directly with nitrogen⁴ to form a nitride of definite composition. The nitrides of indium and thallium have been reported by Fischer and Schroter.⁵ They employed the discharge of an electric arc through a mixture of liquid argon and liquid nitrogen, with the metal serving as electrodes, to cause combination of the elements. In each case a black powder was obtained which appeared to be quite unstable thermally, even at very low temperatures. The data available at the present time are not sufficient, however, to warrant the existence of indic and thallic nitrides as definite compounds. On the other hand, Franklin⁶ has been successful in the preparation of thallos nitride, Tl_3N , in liquid ammonia solution from thallos nitrate and potassium amide.

In view of the position of gallium in third group of elements, one would predict the formation of a nitride possessing properties similar to those of the nitrides of aluminium and indium. The following report shows that gallic nitride resembles aluminium nitride and boron nitride in its apparent stability towards heat, solutions of acids and of bases.

Experimental

Metallic gallium was obtained from germanite ore according to a procedure previously described.⁷ It was purified by fractional crystallization on a platinum wire from the supercooled liquid metal.⁸ Liquid ammonia was thoroughly dried with sodium before being used in any of the experiments.

* Contribution from the George Herbert Jones Laboratory of the University of Chicago.

¹ Stock and Blix: *Ber.*, **34**, 3039 (1901).

² Meyer and Zappner: *Ber.*, **54**, 560 (1921).

³ Friederich and Sittig: *Z. anorg. Chem.*, **143**, 293 (1925).

⁴ Fichter and Spengel: *Z. anorg. Chem.*, **82**, 192 (1913).

⁵ Fischer and Schroter: *Ber.*, **43**, 1465 (1910).

⁶ Franklin: *J. Phys. Chem.*, **16**, 682 (1912).

⁷ See Johnson and Parsons: *J. Phys. Chem.*, **34**, 1210 (1930) for brief description of method and other references.

⁸ Richards and Boyer: *J. Am. Chem. Soc.*, **43**, 274 (1921).

Gallium nitride, GaN, was prepared by the action of ammonia gas on metallic gallium at high temperatures. A boat containing the metal was inserted in a Vitreosil tube which was heated by an electric furnace. The temperature was measured with a Pt,Pt-Rh thermocouple and a Leeds and Northrup Potentiometer Indicator. Reaction was found to proceed slowly at a temperature as low as 700° , but it was necessary to heat the metal to 900 – 1000° for several hours in order to obtain an amount of the nitride sufficient for analysis and study. This procedure was found to be disadvantageous in two respects; (1) metallic gallium is appreciably volatile at temperatures approaching 1000° and consequently distills out of the boat to condense in the cooler regions of the tube without reacting with the ammonia, and (2) the nitride also sublimates at these temperatures to leave the reaction mass. However, the higher temperatures were employed throughout the preparations to obtain appreciable quantities of the nitride although it was found impossible to determine the extent of a given reaction merely by the change in weight of the boat and contents.

When the reaction between metallic gallium and ammonia was completed, the product was analyzed for nitrogen by the distillation of ammonia from a concentrated NaOH solution. The results are shown in Table I under samples listed (1) and (2) which represent two different preparations of the compound. The nitrogen content obtained from the analyses suggests that one atom of gallium is in combination with one atom of nitrogen. The reaction may be expressed as follows:

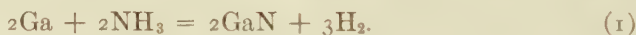


TABLE I

Analysis of Gallic Nitride for Gallium and Nitrogen

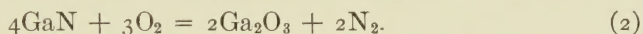
Sample	GaN, g.	Ga (found), g.	Ga (calcd.), g.	N ₂ (found), g.	N ₂ (calcd.), g
(1)	0.0689			0.0115	0.0115
(2)	.1802			.0299	.0301
(3)	.1207			.0209	.0202
(4)	.2070	0.1710	0.1724		
(5)	.2088	0.1746	0.1747		

In order to carry out an analysis of the nitride for nitrogen by the Kjeldahl method, concentrated NaOH solution was used to dissolve the compound. Dilute alkali appeared to have little effect on the nitride, and even the concentrated solution dissolved it slowly on heating. Attempts to recover the gallium from the solution, after the ammonia had been liberated, did not produce satisfactory results due to the presence of appreciable amounts of silica which had been removed from the glass. The possibility of reduction of the nitride at high temperatures with hydrogen to metallic gallium and ammonia was considered in view of the results previously obtained with germanic nitride.⁹

⁹ Johnson: J. Am. Chem. Soc., 52, 5160 (1930).

A small sample of the nitride, 0.1592 g, was heated in a stream of hydrogen at 800° for 24 hours. An examination of the material at the end of this period showed no change in its appearance but a loss in weight of 0.0385 g was noted. On the other hand, a considerable quantity of a grey substance resembling the nitride collected on the walls of the quartz tube outside the heated area. If the nitride were to be completely reduced to metallic gallium without any distillation, the loss in weight would be only 0.0266 g to correspond to the nitrogen. Accordingly, the material remaining in the boat was analyzed for nitrogen by the method indicated above. The results given in Table I (sample 3) show the material to be identical with gallic nitride. This conclusion is substantiated by the fact that the gases discharged from the reaction tube failed to produce any effect on a dilute HCl solution. Evidently, the nitride is slightly volatile at 800°, under a pressure of 1 atmos. of hydrogen, without suffering decomposition or reduction.

Two different methods were found applicable for the determination of gallium. In the first method, the nitride was dissolved in hot, concentrated H₂SO₄, the excess acid was evaporated, the residue dissolved in water, and the gallium was precipitated as hydroxide in the presence of NH₄HSO₃ according to the procedure described by Porter and Browning.¹⁰ The hydroxide was ignited and finally weighed as Ga₂O₃. The gallium content is calculated and shown in Table I (sample 4).¹¹ The second method for the determination of gallium was accomplished by passing oxygen gas over the nitride at high temperatures to form gallic oxide according to the following expression:



The oxidation was found to proceed slowly even at temperatures approaching 900°. At 500° no reaction was observed while at 800° some gallic oxide was noticed after several hours heating. Approximately 30 hours at 875-900° were required to completely oxidize a 0.2 g sample of the nitride. Sublimation of the nitride was not noticed in this experiment; undoubtedly, the oxide which forms at the surface tends to prevent an escape of the more volatile material. The results of the oxidation are given in Table I (sample 5).

All attempts to react metallic gallium directly with nitrogen gas were unsuccessful. Nitrogen was passed over the metal at temperatures ranging from 500-1000° for several days but no indication of a combination of the two constituents was observed.¹²

Properties of Gallic Nitride. Gallic nitride is an exceedingly stable compound. Above 800° it sublimes without decomposition. It is not reduced with

¹⁰ Porter and Browning: J. Am. Chem. Soc., **41**, 1491 (1919).

¹¹ No attempt was made here to determine the nitrogen of the nitride digested with the concentrated H₂SO₄. Undoubtedly, this procedure would allow for analysis of both nitrogen and gallium and thus eliminate the use of concentrated NaOH for the determination of nitrogen.

¹² Observations by Miss E. DeSylvester in this laboratory. Some gallic oxide was formed in this experiment due to traces of oxygen with the nitrogen which escaped removal in being passed over copper at 600°. However, the contents of the reaction chamber failed to show the presence of nitrogen when subjected to analysis.

hydrogen at 900° , but reacts slowly with oxygen at this temperature to form gallic oxide. The nitride is unchanged when treated with dilute and concentrated solutions of HCl, HF and HNO_3 . Hot aqua regia has no effect on the nitride. The compound dissolves slowly in hot, concentrated H_2SO_4 and also in hot, concentrated NaOH. It is stable in air; a sample exposed to air for several weeks showed no change in weight or in appearance. The nitride, as prepared by the reaction between metallic gallium and ammonia gas at high temperatures, appears as a dark grey powder.

Summary

Gallic nitride, GaN, is prepared by reacting metallic gallium with ammonia gas at $900\text{--}1000^{\circ}$. Some of its properties are studied and discussed.

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